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An Analysis of the Effect of Heterogeneous Reaction

Kinetics on the Combustion of Graphite at the Stagnation

Region of a Blunt Body in Hypersonic Flow

28 FEBRUARY 1963

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Prepared for COMMANDER SPACE SYSTEMS DIVISION

UNITED STATES AIR FORCE

Inglewood, California



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AN ANALYSIS OF THE EFFECT OF HETEROGENEOUS REACTION KINETICS ON THE COMBUSTION OF GRAPHITE AT THE STAGNATION REGION OF A BLUNT BODY IN HYPERSONIC FLOW

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ABSTRACT

An approximate analysis is performed for the combustion rate of carbon in air at the stagnation region of a blunt body in hypersonic flow for the intermediate regime of conditions between the reaction-kinetic-limited and the diffusion-limited extremes. The effect of mass addition to the boundary layer caused by the combustion is considered. Combustion rates in the intermediate regime are derived using closed-form approximations for available boundary layer analyses. The results, shown in a generalized form, are valid for arbitrary reaction kinetics and combustion products. The limitations of the series-resistance approach are demonstrated. A numerical comparison of the closed-form results for the mass loss rates in the diffusion-limited regime and the recent results of Scala indicate that the present simplifications are satisfactory for engineering purposes.

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I. INTRODUCTION

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Ballistic re-entry vehicles employing charring-ablator heat shields encounter high surface temperatures during re-entry and the combustion rate of the graphitic-char material is limited by the rate at which oxygen can diffuse through the boundary layer to the burning surface. Lifting-types of re-entry vehicles, however, typically encounter lower heat transfer rates and correspondingly lower surface temperatures. In this case, a graphitic-char material or a graphite may combust at a rate that is more or less dependent upon the heterogeneous reaction-kinetics of the surface combustion process. The degree to which the combustion is dependent upon surface kinetics is a function of the flight condition, the vehicle configuration, the location upon the vehicle, and the chemical make-up and temperature of the surface.

In 1936, Parker and Hottel (Ref. 1) reported on an experimental study in which the combustion rate of graphite and oxygen was measured at values between the reaction-kinetic limit and the diffusion limit. The reaction-kinetic limit may be defined as the combustion rate under conditions where the oxygen concentration at the burning surface is the same as the oxygen concentration far from the surface, i.e., at the edge of the boundary layer. The diffusion-limit is defined as the combustion rate under conditions where the oxygen concentration at the burning surface is essentially zero (for practical ranges of wall temperatures). The diffusion-limit is found to vary only slightly with surface temperature, due to small changes in boundary layer transport properties. The reaction-kinetic limit possesses an extreme dependence on surface temperature, usually expressed as an exponential after Arrhenius.

Parker and Hottel found their data indicated that the combustion rate of carbon in the intermediate range of surface oxygen concentrations could be expressed by a relation analogous to that for the flow of electrical current

through two resistances in series. They identified the inverse of the reaction-kinetic limited combustion rate as a chemical resistance and the inverse of the diffusion-limited combustion rate as a diffusion resistance. In 1947, Frank-Kamenetskii (Ref. 2) presented a simplified analysis of combustion in the intermediate regime, which ignored the effect on the boundary layer characteristics of mass transfer from the wall. According to Frank-Kamenetskii's analysis, the data of Parker and Hottel conformed to fractional-order rather than first-order kinetics as they had originally deduced.

In 1961, Moore and Zlotnick (Ref. 3) performed an approximate analysis of the combustion of graphite in the intermediate regime for a unity Lewis number, using the reaction-kinetic-data of Blyholder and Eyring (Ref. 4). They considered the case of a boundary layer in which CO evolving from the heterogeneous reaction diffused toward a gas reaction zone at some arbitrary distance from the surface where it is reacted with oxygen to form CO₂. The CO₂ then diffused back to the graphite surface to react heterogeneously with graphite to form gaseous CO.

In 1962, Scala (Ref. 5) reported the results of numerical boundary layer calculations for the combustion rate of graphite at the stagnation point of a hemisphere in hypersonic flow. He considered the cases of a boundary layer in which gas-phase reactions were prohibited (frozen) and a boundary layer in which gas-phase reactions proceeded at a rate sufficient to cause local thermochemical equilibrium at all locations.

In the intermediate regime (between the rate-limited and diffusion-limited combustion), Scala treated the kinetics as being of one-half order and calculated the combustion rate by the series-resistance method.

Scala's numerical analysis provides an accurate solution of the diffusion-limited combustion rate and an approximate solution of the intermediate-regime combustion rate. His intermediate regime results must be considered only approximate since it has not been shown that the series-resistance method utilized may be applied for reactions of arbitrary order, different from unity.

In this report, the problem analyzed by Scala will be studied, for the frozen boundary layer case, by the use of approximate but closed-form solutions of the stagnation-point boundary layer equations. The purpose of the analysis is to show the general coupling features of the oxygen diffusion, the surface reaction kinetics, and the mass transfer of combustion products with regard to the overall combustion rate. The accuracy of the series-resistance method will be investigated. In addition, it will be shown that the present approximate results can predict the diffusion-limited ablation rates within satisfactory accuracy.

II. ANALYSIS

The problem of a heterogeneous reaction at a wall undergoing a transition from a dependence upon surface kinetics to a dependence upon boundary layer diffusion, for the case of wall-catalyzed recombination of dissociated atoms, was treated by Chung (Ref. 6) in 1959. In that analysis, Chung investigated the effect of air injection through a porous wall of arbitrary catalytic efficiency on the nature of the transition from the reaction-kinetic limit to the diffusion limit of wall-catalyzed oxygen recombination rates. A direct analogy between the graphite-combustion problem and the wall-catalyzed atom recombination problem exists for the case where the boundary layer conditions prohibit gas-phase reactions. The essential features of the analysis of Reference 6 will be utilized in the development which follows. It is convenient to choose a flow configuration for which satisfactory solutions for diffusion and heat transfer are available. Such a configuration is the stagnation region of an axisymmetric or two-dimensional blunt body in hypersonic flow.

The fundamental equations for a frozen laminar boundary layer at the stagnation region sketched in Figure 1 are

Continuity:

$$\frac{\partial}{\partial \mathbf{x}} \left(\rho \mathbf{u} \mathbf{r}_{o}^{\epsilon} \right) + \frac{\partial}{\partial \mathbf{y}} \left(\rho \mathbf{v} \mathbf{r}_{o}^{\epsilon} \right) = 0^{*} \tag{1}$$

Momentum:

$$\rho u \left(\frac{\partial u}{\partial x} \right) + \rho v \left(\frac{\partial u}{\partial y} \right) = \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) - \frac{\partial P}{\partial x}$$
 (2)

^{*}Note: $\epsilon = 0$ for a two-dimensional body, 1 for a rotationally-symmetric body.

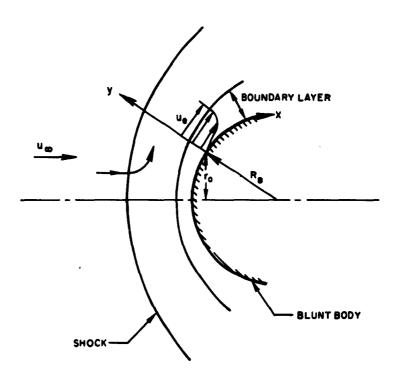


Figure 1. Physical Model

Energy:

$$\rho u \left(\frac{\partial h}{\partial x} \right) + \rho v \left(\frac{\partial h}{\partial y} \right) = \frac{\partial}{\partial y} \left(\frac{k}{C_p} \frac{\partial h}{\partial y} \right) - \frac{\partial}{\partial y} \left[\mu \left(\frac{1}{P_r} - 1 \right) \frac{\partial}{\partial y} \left(\frac{u^2}{2} \right) \right]$$
(3)

Diffusion:

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$$\rho u \left(\frac{\partial c}{\partial x} \right) + \rho v \left(\frac{\partial c}{\partial y} \right) = \frac{\partial}{\partial y} \left(\rho D \frac{\partial c}{\partial y} \right) \tag{4}$$

The following transformation relations are utilized:

$$\rho u r_{o}^{\epsilon} = \frac{\partial \psi}{\partial y}$$
 (5a)

$$\rho v r_{o}^{\epsilon} = -\frac{\partial \psi}{\partial x} \tag{5b}$$

$$s = \int_0^x \rho_e \mu_e u_e r_o^{2\epsilon} dx$$
 (5c)

$$\eta = \frac{u_e r_o^{\epsilon}}{\sqrt{2sC}} \int_0^y \rho \, dy \tag{5d}$$

$$\frac{u}{u_e} = f'(\eta) \tag{5e}$$

$$f(\eta) = \frac{\psi}{\sqrt{2\pi C}} \tag{5f}$$

Where C is assumed to be constant in the transformation. Also, it will be assumed that Pr and Sc numbers are constant across the boundary layer.

The additional quantities g and Z are defined as

$$g(\eta) = \frac{h(\eta)}{h_e}$$
 (5g)

$$Z(\eta) = \frac{c_1(\eta)}{c_{1,e}}$$
 (5h)

where c₁ is the concentration of the gaseous reactant of interest, oxygen. The continuity equation is satisfied by the stream function transformation, and the momentum, energy, and diffusion equations transform to

$$f''' + ff'' = \frac{2s}{u_e} \left(\frac{du_e}{ds} \right) \left(f'^2 - \frac{\rho_e}{\rho} \right)$$
 (6)

$$fg' + \frac{1}{Pr} g'' = \frac{u_e^2}{h_e} (\frac{1}{Pr} - 1) (f'f'')$$
 (7)

$$fZ' + \frac{1}{Sc}Z'' = 0$$
 (8)

Lees (Ref. 7) showed that the terms on the right-hand sides of Eqs. (6) and (7) can be neglected without appreciable error if the wall surface is highly cooled. This condition is fulfilled at wall temperatures of practical interest for graphite materials in the hypersonic regime. Thus the equations simplify to

$$f''' + ff'' = 0 \tag{9}$$

$$\mathbf{f}\mathbf{g}^{\dagger} + \frac{1}{\mathbf{P}\mathbf{r}}\mathbf{g}^{\dagger} = 0 \tag{10}$$

$$fZ' + \frac{1}{Sc} Z'' = 0 {(11)}$$

The boundary conditions to be imposed for the solution of the momentum and diffusion equations are

$$f(0) = f_{yy} \tag{12a}$$

$$f'(0) = 0 \tag{12b}$$

$$f'(\infty) = 1 \tag{12c}$$

$$Z(\infty) = 1 \tag{12d}$$

$$Z(0) = Z_{w} (12e)$$

It is noted that f_w and Z_w are not arbitrary, but depend on the surface chemical reaction. The frozen energy equation, (10), will not be solved, but solutions may be found in References 6 and 8.

The rate of mass loss from a burning surface is expressed as the Arrhenius form

$$\dot{m}_{w} = k_{1}(P_{1,w})^{n} e^{-E_{a}/RT_{w}}$$
 (13)

where k_1 is the frequency factor, $P_{1,w}$ is the partial pressure of the gaseous reactant at the wall, and n is the order of reaction. The partial pressure

 $P_{1,w}$ can be expressed in terms of the total pressure P_{w} , molecular weight ratio $(\overline{M}/M_{1})_{w}$, and oxygen reactant concentration at the wall $c_{1,w}$.

$$P_{1,w} = P_w \left(\frac{\overline{M}}{M_1}\right)_w c_{1,w}$$
 (14)

The frequency factor and the exponential term are combined as k_w.

$$k_{w} = k_{1} e^{-E_{a}/RT}$$
 (15)

Taking the static pressure as constant across the boundary layer, we may express the mass loss rate as

$$\dot{m}_{w} = k_{w} \left[P_{e} \left(\frac{\overline{M}}{M_{1}} \right)_{w} \right]^{n} c_{1, w}^{n}$$
(16)

The stoichiometric relation for heterogeneous combustion is written as

$$n_{w}M_{w} + n_{1}M_{1} + \sum_{p} n_{p}M_{p}$$
 (17)

where w refers to carbon, 1 to oxygen, and p to the product species. Thus the gaseous reactant transport rate corresponding to the wall mass loss rate is

$$\dot{m}_1 = \frac{n_1 M_1}{n_w M_w} k_w \left[P_e \left(\frac{\overline{M}}{M_1} \right)_w \right]^n c_{1,w}^n$$
 (18)

Equating this to the net transport rate of gaseous reactant at the wall, the boundary condition is obtained for the diffusion equation at y = 0

$$\rho_{\mathbf{w}} \mathbf{D}_{\mathbf{w}} \left(\frac{\partial c_1}{\partial \mathbf{y}} \right)_{\mathbf{w}} - \rho_{\mathbf{w}} \mathbf{v}_{\mathbf{w}} c_{1, \mathbf{w}} = \frac{\mathbf{n}_1 \mathbf{M}_1}{\mathbf{n}_{\mathbf{w}} \mathbf{M}_{\mathbf{w}}} \mathbf{k}_{\mathbf{w}} \left[\mathbf{P}_{\mathbf{e}} \left(\frac{\overline{\mathbf{M}}}{\mathbf{M}_1} \right)_{\mathbf{w}} \right]^{\mathbf{n}} c_{1, \mathbf{w}}^{\mathbf{n}}$$
(19)

Using the relations

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$$r_o(x) = x$$

$$\rho_e \mu_e = (\rho_e \mu_e)_s$$

$$u_e = \beta x$$

$$\rho_w v_w = -f_w \sqrt{(1 + \epsilon)\beta(\rho_e \mu_e)_s} C$$

for the stagnation region, and the transformation relations (5), the diffusion boundary condition becomes

$$Z'(0) = Sc \begin{cases} \frac{n_1 M_1}{n_w M_w} k_w \left[P_e \left(\frac{\overline{M}}{M_1} \right)_w \right]^n c_{1,e}^{n-1} \\ \frac{\sqrt{(1+\epsilon)\beta(\rho_e \mu_e)_s C}}{\sqrt{(1+\epsilon)\beta(\rho_e \mu_e)_s C}} - f_w Z^{1-n}(0) \right] Z^n(0) \end{cases}$$
 (20)

Since the wall temperature and the parameters associated with it are assumed to be invariant with x, similarity is not impaired by the inclusion of the heterogeneous chemical kinetics in the boundary condition at the reacting surface. It is convenient to define a Damköhler number D_m as

$$D_{m} = \left\{ \frac{\frac{n_{1}M_{1}}{n_{w}M_{w}} k_{w} \left[P_{e} \left(\frac{\overline{M}}{M_{1}} \right)_{w} \right]^{n} c_{1,e}^{n-1}}{\sqrt{(1+\epsilon)\beta(\rho_{e}\mu_{e})_{s}C}} \right\}$$
(21)

This parameter characterizes the ratio, for a unit mass of oxygen, of the diffusion time at the diffusion limit to the reaction time at the reaction-kinetic limit, and allows the following, more compact, version of equation (20):

$$Z'(0) = Sc \left[D_m - f_w Z^{1-n}(0)\right] Z^n(0)$$
 (22)

The application of boundary condition (12d) to the diffusion equation (11) leads to the solution

$$1 - Z(0) = \frac{Z'(0) \int_{0}^{\infty} [f''(\eta)]^{Sc} d\eta}{[f''(0)]^{Sc}}$$
 (23)

For low values of f_w , the following relations furnish good approximations of the numerical results of References 6 and 9 for air boundary layers:

$$\int_{0}^{\infty} [f''(\eta)]^{Sc} d\eta \simeq C_{1} \qquad f_{w} < 0.2$$
 (24)

$$[f''(0)]^{Sc} \simeq C_2 + C_3 f_w \qquad f_w < 0.2$$
 (25)

where for
$$Sc = 0.72$$
 (Ref. 8)* and for $Sc = 0.514$ (Ref. 6)
$$C_1 = 1.391 C_1 = 1.825$$

$$C_2 = 0.580 C_2 = 0.678$$

$$C_3 = 0.610 C_3 = 0.485$$

These are Low's results, numerically modified to correspond to the present nomenclature. There is a factor of $\sqrt{2}$ involved between the present f and η and those of Low. These factors are pointed out by Chung (Ref. 6).

When an injected specie has a molecular weight much different from that of air, these results must be modified; however, the CO and $\rm CO_2$ combustion products for this problem have molecular weights sufficiently close to air that such modifications would be small. Also, the $\rm f_w$ values in this problem are characteristically below 0.2 even at the diffusion limit. Therefore, these approximations are considered applicable within reasonable accuracy.

By applying the boundary condition at the wall (Eq. 22) to the diffusion equation solution (Eq. 23) and expressing f_{w} in terms of the Damköhler parameter, we obtain, after rearranging terms,

$$1 - Z(0) = \frac{Sc \left[1 + \frac{n_{\mathbf{w}} M_{\mathbf{w}}}{n_{1} M_{1}} c_{1, e} Z(0)\right]}{\frac{C_{2}}{C_{1} D_{\mathbf{w}} Z^{n}(0)} - \frac{C_{3} n_{\mathbf{w}} M_{\mathbf{w}} c_{1, e}}{C_{1} n_{1} M_{1}}}$$
(26)

Now, for the given values of Sc and D_m, and for the given products of combustion, Eq. (26) gives the wall concentration of oxygen. The combustion rate can then be obtained from Eqs. (16) and (21).

The diffusion-limited combustion rate may be calculated by letting $Z(0) \rightarrow 0$ in Eq. (26) and solving for $D_m Z^n(0)$. Then the combustion rate is

$$\dot{m}_{w,d.l.} = \frac{n_w M_w}{n_1 M_1} \sqrt{(1+\epsilon)\beta(\rho_e \mu_e)_s C} c_{1,e} D_m Z^n(0)$$
 (27a)

or

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$$\dot{m}_{w,d.l.} = \frac{c_{l,e} \sqrt{(1+\epsilon)\beta(\rho_e \mu_e)_g C}}{\frac{C_3 c_{l,e}}{C_2} + \frac{C_1 Sc n_1 M_1}{C_2 n_w M_w}}$$
(27b)

III. RESULTS AND COMPARISON WITH OTHER INVESTIGATORS

The first point to be examined is that of the accuracy of this method of calculating the diffusion-limited mass loss rate. The recent results of Scala (Ref. 5), obtained using accurate numerical solutions of the boundary layer differential equations, afford a good reference. It will be assumed that the ratio of carbon monoxide-to-carbon dioxide gas produced by the combustion is given by the equilibrium relation.

$$C(s) + CO_2(g) \stackrel{\leftarrow}{\Rightarrow} 2CO(g)$$

The equilibrium constant for this relation, as used by Scala, is

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$$K_{p} = \frac{(P_{CO})^{2}}{(P_{CO_{2}})}$$
, $M_{10}K_{p} = 8.80 - \frac{15030}{T_{OR}}$

Lees (Ref. 7) has suggested that the Schmidt number for boundary layers adjacent to burning carbon surfaces is between 0.5 and 0.7. Therefore, the relations approximating the results of References 6 and 9 for Schmidt numbers of 0.514 and 0.72, respectively, furnish useful solutions for comparison.

Figure 2 shows the diffusion-limited mass loss rate resulting from the solution of Eq. (27b) for the following flight conditions of Reference 5: vehicle velocity, 20,000 ft/sec; altitude, 100,000 ft. The numerical results of Reference 5 are also shown in Figure 2. A large increase in mass loss rate occurs as wall temperature is raised from 1000°R to 2000°R, due to the change of the equilibrium product from primarily CO₂ to primarily CO gas. The small variation in mass loss rate occurring at temperatures higher than 2000°R is due to changes in the density and viscosity in the boundary layer.

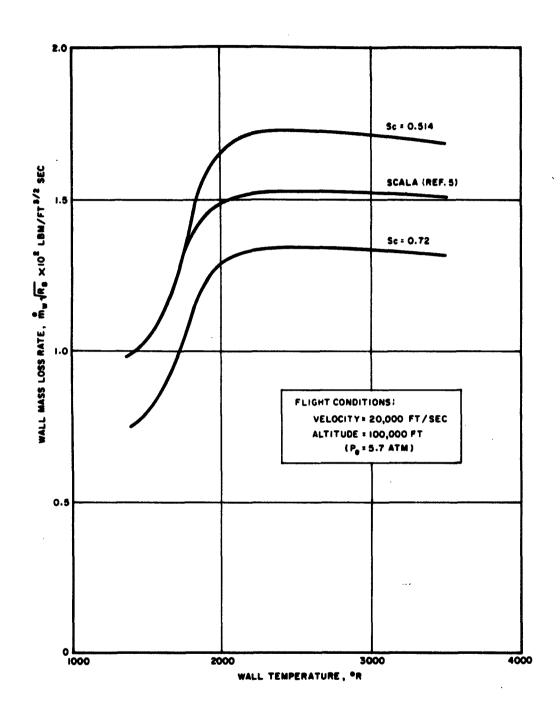


Figure 2. Comparison of Graphite Mass Loss Rates at the Diffusion Limit

The results of Scala correspond to the solution for Sc = 0.514 at low wall temperatures and to a solution that would result using a Schmidt number midway between 0.514 and 0.72 at the higher wall temperatures. It is apparent that the simplified closed-form solutions can yield satisfactory engineering results for the diffusion-limited mass loss rates since errors up to fifteen percent (Ref. 5), due to uncertainties in transport properties, are possible in all results shown in Figure 2.

In the intermediate regime, it is not necessary to specify particular numerical values for the Arrhenius relation since the Damköhler number includes this factor in the general results. It is, however, necessary to specify the order of reaction, n, and the product of the reaction. As discussed by Scala (Ref. 5), there is considerable disagreement in the literature on combustion as to the order of reaction for O₂-graphite combustion. One-half order kinetics are widely utilized, however, and the Scala (Ref. 5) and Moore and Zlotnick (Ref. 3) articles both incorporated that order. Hottel found experimentally that the order was close to unity. The effective combustion product can range from primarily CO to primarily CO₂. To accommodate this range of reaction orders, products, and the expected variation of Schmidt number, Eq. (26) was solved for n = 1 and 1/2; CO and CO₂ products; and Sc = 0.514 and 0.72.

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The results of this calculation, shown in Figure 3, indicate the dimensionless concentration of oxygen at the wall versus the Damköhler number. The average molecular weight of the gas mixture at the reacting surface, $(\overline{M})_{W}$, was taken as that of air, since nitrogen is the predominant specie and the molecular weights of the combustion products are not far different from oxygen. The results for a CO_2 product are shown only as perturbations from the CO product curves. The differences between CO_2 and CO product results are small for given reaction orders and Schmidt numbers. The present results for unity reaction order are seen to require an increase of four orders of magnitude in Damköhler number in order to lower the oxygen

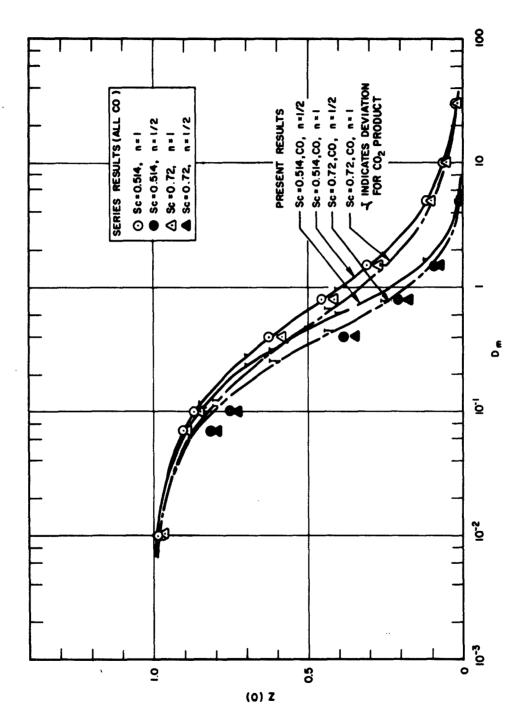


Figure 3. Oxygen Concentration at the Wall in the Intermediate Regime

concentrations at the wall from 99 percent to 1 percent of the free-stream concentration. A reaction order of one-half requires an increase in D_m of only three orders of magnitude for a similar transition. The different Schmidt numbers at a given reaction order show results converging at the extremes and differing a small amount at intermediate Damköhler numbers. Results calculated from relations derived in the Appendix using the series-resistance method are also shown in Figure 3 at particular Damköhler values. It is noted that the series-resistance method leads to oxygen concentrations that are approximately correct for unity reaction order but quite inaccurate for a one-half reaction order. The series results are not exactly valid even for unity reaction order because the modifications to the boundary layer diffusion rates due to mass addition are not adequately represented in the intermediate regime.

The fractional mass loss rates, defined as the ratio of the wall mass loss rate to the wall mass loss rate at the diffusion limit, were obtained from the results of Figure 3 and Eqs. (16) and (27b), and are shown in Figure 4 for a CO product. The mass loss rates given by the reaction-kinetic limit and by the series method are shown for reference. The present results require $D_{\rm m}$ changes of the same order as in Figure 3 to accommodate a 1-to-99 percent transition, and again the series result is adequate for n = 1 and inadequate for n = 1/2 reaction order.

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The fundamental reason for the failure of the series-resistance method when utilized for a reaction order of one-half is that the reaction-kinetic limit then does not depend linearly upon the oxygen concentration, whereas the diffusion-limit does show a linear dependence. A series-resistance calculation is predicated upon the quantity of flow having a linear dependence on the potential across each resistance.

There exist considerable uncertainties in the values of the reaction-kineticconstants for the combustion of the various grades of graphites with oxygen,

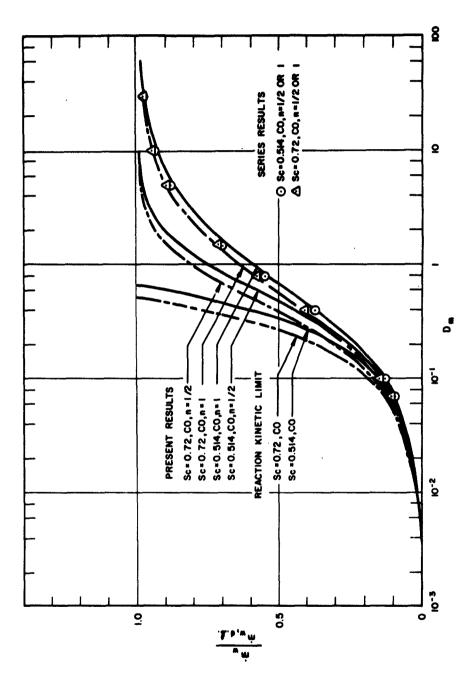


Figure 4. Fractional Mass Loss Rate in the Intermediate Regime

and in the proportions of GO and GO₂ produced by the reaction. It is felt that the present results are sufficiently simple and general to furnish a useful method for calculating combustion rates with any kinetics and products that may be found appropriate. The question of the proportions of GO and GO₂ produced in the intermediate regime is at present unanswered. Although the equilibrium written between carbon, carbon dioxide, and carbon monoxide is a reasonable postulate for the diffusion-limited condition, it may become invalid in the intermediate regime. The reaction-kinetics of the carbon-carbon dioxide reaction (as described, for instance, in Ref. 2) may then become significant. Thus, the numerical calculation of combustion rates in the intermediate regime, at the present time, must be performed for the limiting cases of either GO or GO₂ product formation to show the possible ranges of these results.

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IV. CONCLUSION

The simultaneous effects of heterogeneous reaction-kinetics and oxygen diffusion to a burning graphite stagnation surface may be described by a simple relation (Eq. 26), which utilizes closed-form approximations to available boundary layer diffusion solutions and a Damköhler number. The Damköhler number characterizes the ratio of the time for a quantity of oxygen to diffuse to the surface to the time for a quantity of oxygen to chemically react with the surface.

The use of closed-form approximations to available boundary layer solutions allows rapid estimation of diffusion-limited combustion rates, within reasonable engineering accuracy.

The relations derived for the oxygen concentration at the burning graphite surface in the intermediate regime (Eq. 26) may be utilized for any reaction order, reaction-kinetic constants, or reaction products that may be considered appropriate.

The proportions of carbon monoxide and carbon dioxide products formed by combustion in the intermediate regime are presently in question; therefore, the numerical value of the carbon mass loss rate has been calculated only for the limiting cases of CO or CO₂ product formation. An investigation is now in progress to extend this analysis to determine the effective ratio of carbon monoxide to carbon dioxide produced by the heterogeneous reaction.

A series-resistance approach to the intermediate regime is adequate for unity reaction order providing the diffusion-limited mass loss rate takes proper account of the effects of mass addition. The series approach is inadequate for a reaction order of one-half.

APPENDIX

Derivation of Results of the Series-Resistance Method

The basic relation postulated by this method is

$$\frac{1}{\dot{\mathbf{m}}_{\mathbf{w}}} = \frac{1}{\dot{\mathbf{m}}_{\mathbf{w}, \mathbf{r}, 1}} + \frac{1}{\dot{\mathbf{m}}_{\mathbf{w}, \mathbf{d}, 1}}$$

where r.1. refers to the reaction-kinetic limit where Z(0) = 1 and d.1. refers to the diffusion limit where Z(0) is essentially zero. When the relations derived in Eqs. (16) and (27b) are inserted, these terms become

$$\frac{1}{k_{\mathbf{w}} \left[P_{\mathbf{e}} \left(\frac{\overline{M}}{M_{1}} \right)_{\mathbf{w}} \right]^{n} c_{1, \mathbf{w}}^{n}} = \frac{1}{k_{\mathbf{w}} \left[P_{\mathbf{e}} \left(\frac{\overline{M}}{M_{1}} \right)_{\mathbf{w}} \right]^{n} c_{1, \mathbf{e}}^{n}} + \frac{\frac{1}{c_{1, \mathbf{e}} \sqrt{(1 + \epsilon)\beta(\rho_{\mathbf{e}} \mu_{\mathbf{e}})_{\mathbf{g}} C}}}{\frac{C_{3} c_{1, \mathbf{e}}}{C_{2}} + \frac{C_{1} S c_{1} M_{1}}{C_{2} n_{\mathbf{w}} M_{\mathbf{w}}}}$$

Rearranging,

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$$\frac{1}{z^{n}(0)} = 1 + \frac{k_{w} \left[P_{e} \left(\frac{\overline{M}}{M_{1}} \right)_{w} \right]^{n} c_{1,e}^{n-1}}{\sqrt{(1+\epsilon)\beta(\rho_{e}\mu_{e})_{g}C}} \left(\frac{C_{3}c_{1,e}}{C_{2}} + \frac{C_{1}Sc_{1}M_{1}}{C_{2}n_{w}M_{w}} \right)$$

By definition of the Damköhler number (Eq. 21), this becomes

$$\frac{1}{z^{n}(0)} = 1 + D_{m} \left(\frac{C_{3}c_{1,e}^{n} M_{w}^{M}}{C_{2}^{n} M_{1}^{M}} + \frac{C_{1}Sc}{C_{2}} \right)$$

or

$$Z(0) = \left[\frac{1}{1 + D_{m} \left(\frac{C_{3} c_{1,e}^{n} M_{w}}{C_{2}^{n} M_{1}} + \frac{C_{1} S c}{C_{2}} \right)} \right]^{1/n}$$

This derivation has been made only for the purpose of allowing a comparison with the present results. As shown in the main body of this report, the series method leads to erroneous results.

NOMENCLATURE

c	mass fraction concentration
С	$(\rho_{\mathbf{w}}^{\mu}_{\mathbf{w}}/\rho_{\mathbf{e}}^{\mu}_{\mathbf{e}})^{0.2}$
c_1, c_2, c_3	constants defined in Eqs. (24) and (25)
C _p	specific heat
D	diffusion coefficient
$D_{\mathbf{m}}$	modified Damköhler number defined in Eq. (21)
Ea	activation energy
f	transformation variable, $-\rho_w v_w / \sqrt{(1+\epsilon)\beta(\rho_e \mu_e)_s C}$
g	dimensionless enthalpy
h	frozen enthalpy
k	thermal conductivity
k ₁	frequency factor
k _w	specific reaction rate
$\dot{\mathbf{m}}_{\mathbf{w}}$	mass loss rate of surface
M	molecular weight
n	reaction order or stoichiometric coefficient
P	static pressure, atm
Pr	Prandtl number
ro	radial coordinate
R	universal gas constant
RB	body nose radius
	transformation variable

NOMENCLATURE (Continued)

Sc	Schmidt number, $\mu/\rho D_{12}$
T	temperature, absolute
u	velocity component parallel to wall
v	velocity component normal to wall
×	coordinate parallel to wall surface
у	coordinate normal to wall surface
Z	oxygen concentration ratio
β	external free stream velocity gradient
•	exponent for body shape
η	similarity variable
μ	viscosity
ρ	density
ψ	stream function
C.1	1 Company and the

Subscripts and Superscripts

e	edge of boundary layer
w	at the wall surface
\Box	average
1	gaseous reactant
d . 1.	diffusion limit
r. l.	reaction-kinetic limit
∞	vehicle

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